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Observations on the Rare Earths:

A Study of Some Methods for the Separation of Holmium

OBSERVATIONS ON THE RARE EARTHS: A STUDY OF SOME METHODS FOR THE SEPARATION OF HOLMIUM

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY LEONARD FRANCIS YNTEMA

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Recommendation concurred in:*

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I. Introduction.

This work was undertaken in order to study the means by which holmium may be separated from yttrium and other yttrium earths that fall near it in the fractionation of the bromates.[1] Much of the material employed was secured from a series described by Engle and Balke,[2] that had been obtained from several mineral sources.

II. History of Holmium.

In 1879 Cleve[3] announced, as a result of his endeavor to extract the coloring principle from erbium, the discovery of two new rare earths, thulium and holmium, each with a characteristic absorption spectrum. Separation was secured by fractional decomposition of the nitrates. Holmium was named from the latinized name of Stockholm, near which city many of the rare earth minerals are found. The atomic weight was announced as being less than 108 (R O). Soret[4] pointed out that Cleve's holmium was identical with a new earth the discovery of which he had announced[5] the year previous and which he had designated as X.

A few years later, Lecoq de Boisbaudran[6] showed that, by means of fractional precipitation with potassium sulphate and alcohol, the holmium could be divided into two individuals, the less

1. James and Bissel, Jour. Amer. Chem. Soc., 36, 2060 (1914)
2. Ibid. 39, 53 (1917)
3. Compt. rend., 89, 478 (1879); Chem. News, 40, 125 (1879)
4. Compt. rend., 89, 521 (1879); Chem.News, 40, 147 (1879)
5. Compt. rend., 87, 578 (1878); Chem. News, 37, 237 (1878) Arch. Sc. Phys. et Nat., 63, 99 (1878)
6. Compt. rend., 102, 1003 (1886); Chem.News, 53, 265 (1886)

basic of which was given the old name holmium and the other dysprosium.

Hofmann and Krüss,[1] using fractional precipitation with aniline, were unable to secure fractions having either a constant absorption spectrum or atomic weight. They concluded, as had Krüss and Nilson[2] who studied holmium obtained from different sources and found the spectra of the different samples to vary, that holmium was a mixture of several individuals.

Forsling,[3] subjecting the chloride to fractional crystallization in hydrochloric acid or to fractional deliquesence, did not secure fractions with identical spectra.

Langlet[4] subjected material consisting chiefly of holmium, yttrium, and erbium to many methods of fractionation. The crystallization of the chloride in twenty percent hydrochloric acid gave the best results. The fractions at the insoluble end of his series were practically erbium and yttrium free, although there was probably some dysprosium and terbium present.

For the separation of dysprosium and holmium, Urbain[5] employed the crystallization of the hydrated nitrates after the ethyl sulphate crystallization was no longer practical because of the degree of hydrolysis. He was not able to secure holmium free from either dysprosium or yttrium.

In 1911 Holmberg[6] published a paper on the purification and atomic weight of holmium. He subjected earth oxalates from

1. Z. anorg. Chem., 5, 407(1893)
2. Ber., 20, 2134(1887)
3. Bihang. K. Svenska Vet. Akad. Handl. 28, II, No.1. 1-21 (1902) Abstr. Chem. Soc., 86, II, 176(1904)
4. Arkiv. för Kemi. Min. ock Geol. 2, Nr. 32, 1(1907). Chem. Centr. 78, 1308 (1907)
5. J. Chim. phys., 4, 31 (1906); Ann. Chim., Ser. 8, 18, 222(1909)
6. Z. anorg. Chem., 71, 226 (1911)

euxenite to fractional recrystallization and thus collected the dysprosium, holmium, yttrium, and erbium and a small amount of the terbium group elements in the middle fractions. The holmium along with the terbium earths was concentrated in the insoluble end of a m-nitrobenzenesulphonate series. Recrystallization of the nitrates in the presence of bismuth nitrate removed practically all the europium, samarium, and erbium. The fractions at the insoluble end of the series were converted into oxalates and dissolved in ammonium oxalate, one hundred fractionations concentrated the holmium and erbium in the most soluble fractions. To remove the last traces of erbium, dysprosium, and terbium, the nitrates were again employed. After more than four hundred series of fractionations and further purification of the holmium rich portion of the series by precipitation with ammonium hydroxide and by fusion of the sulphates, material with a constant atomic weight was obtained. The presence of small amounts of dysprosium and erbium was shown by the absorption spectrum. The mean of several atomic weight determinations, made by converting the oxide into the anhydrous sulphate, gave the value 163.45.

III. Separation of the Cerium and Yttrium Groups.

A portion of the work undertaken consisted in the extraction of the rare earths from the mineral gadolinite. The finely powdered mineral was extracted with dilute hydrochloric acid, the extraction being continued until the earths were practically all removed. The solution which contained, besides the

rare earths, beryllium and iron, was treated with a hot concentrated oxalic acid solution. The precipitated earth oxalates were washed several times by decantation, agitation being effected by a blast of air.

For the separation of the cerium and yttrium groups the plan outlined by James[1] was followed, which depends on the relative insolubility of the cerium earths in the presence of a strong solution of sodium sulphate. Ten kilos of oxalates were converted into the sulphates by mixing with sufficient concentrated sulphuric acid to form a crumbly mass and igniting in a porcelain dish or on an asbestos pad until sulphur trioxide fumes ceased coming off. Since the anhydrous sulphates are appreciably more soluble in cold water than in warm, the sulphates in powdered form were sprinkled on the surface of water kept at 7^o or 8^o C. and were stirred in, care being taken to avoid the addition in lumps, because of a partial hydrolysis that might be caused by heat of dilution. A portion that did not dissolve was treated with sulphuric acid, reignited and dissolved. During this solution sixty grams hydrolyzed and became insoluble.

Sodium sulphate in small quantities was added until the absorption showed that neodymium was practically removed. The solution, contained in a large stone jar, was agitated by a mechanical stirring device. The precipitate, consisting of the double sodium sulphates of the cerium group elements, was allowed to settle and after decanting the supernatant liquid, was drained on a Büchner funnel and set aside. The solution, containing the yttrium group elements, was treated with oxalic

1. Journ. Amer. Chem. Soc., 34, 757 (1912)

acid and the oxalates, after washing to remove as much as possible of the alkali, were ignited to the oxides in an assay furnace.

IV. Separation of Cerium.

A qualitative test applied at this point showed the presence of some cerium. Since cerium interferes with the fractionation of the earths as bromates because of its tendency to form an insoluble basic bromate upon oxidation to the ceric state, it was thought advisable to remove it at this point.

The method, described by James,[1] of oxidizing the cerium with potassium bromate was employed. The oxides were dissolved in nitric acid and the solution was evaporated to a sirupy consistency. Neutralization was secured by adding lumps of marble. The solution contained in granite pans, was kept at constant volume during the boiling by the use of a constant level flask. Potassium bromate was added in small quantities until the earth solution no longer gave the hydrogen peroxide test for cerium. The cerium precipitated as a red basic salt that was hard to filter because of its tendency to clog the filter paper. The small quantity of this precipitate formed, indicated that the separation of the cerium group from the yttrium had been practically complete. The solution was diluted to a large volume and ammonium hydroxide added to precipitate the earths, as a means of removing the alkali metals added in the form of sodium sulphate and potassium bromate. The hydroxides, after several

1. Loc. cit.

washings, were dissolved in nitric acid, and the earths precipitated as the oxalates.

V. Preparation of the Bromates.

The earths were prepared for the preliminary separation of the yttrium group to be effected by the bromate method of James[1]. The oxalates were converted into anhydrous sulphates and dissolved according to the method described above. The rather concentrated sulphate solution was added drop by drop to a hot saturated solution of barium bromate in contact with undissolved salt. Agitation was secured by a mechanical stirring device. In order that the reaction might run well, enough barium bromate was kept in solution to make the precipitation of barium sulphate instantaneous. If the earth sulphates were in excess in the solution, a precipitate of barium sulphate around each particle of the solid barium bromate would have prevented a large amount from being utilized and the reaction would have proceeded to completion very slowly. The solution, containing a small amount of barium bromate along with the earth bromates, was filtered free from barium sulphate and evaporated to a concentration such that on cooling a half of the salts crystallized out.

VI. Determination of Equivalents.

For computing the mean atomic weights of members of a series the method of Gibbs[2] for determination of equivalents was

1. Loc. cit.

2. Amer. Chem. Journ. 15, 546 (1893)

employed. A one or two gram portion of the oxide is dissolved in nitric acid and the solution diluted. From this hot solution the oxalates are precipitated by adding a solution of pure oxalic acid, that was obtained by recrystallizing the ordinary C.P. acid and drying in a centrifugal machine. The oxalates are washed several times with hot water and dried for four hours at 110° in an air oven. After thorough mixing of the sample, two portions are weighed out, one for ignition to the oxide in a platinum crucible for the determination of the earth oxide and the other for the determination of the oxalic acid. The latter portion is dissolved in 2.5 normal sulphuric acid and titrated with 0.1 normal potassium permanganate. The atomic weights are calculated from the formula, At. Wt. $= \dfrac{\% R_2O_3 \times 108}{\% C_2O_3} - 24$.

VII. Fractional Hydrolysis of the Phthalates.

Urbain[1] suggested that the best method for serparating holmium and yttrium would depend on the difference in basicity of the two elements. Meyer and Wuorinen[2] employed the fractional hydrolysis of the phthalates for the separation of yttrium from the less basic members of the yttrium group. It was thought that a modification of this method could be employed for the separation of holmium from the more basic yttrium.

Material for this fractionation was secured from a bromate series described by Engle and Balke.[3] Fraction 24, consisting

1. Ann. Chim., Ser. 8, <u>18</u>, 222 (1909)
2. Z anorg. Chem., <u>80</u>, <u>7</u> (1913)
3. Loc. cit.

of approximately sixty eight grams of a light yellow oxide, was shown by the absorption spectrum of a concentrated solution to be free from all earths yielding absorption bonds excepting holmium. The atomic weight 97.7 showed a high yttrium content.

The oxides for this fractionation were dissolved in nitric acid and the hydroxides precipitated from a dilute hot solution by the addition of ammonium hydroxide. After being washed several times, the suspended hydroxides were added, a small portion at a time, to phthalic acid suspended in water. The phthalic acid was kept in excess to prevent the formation of an extremely insoluble basic compound. Meyer and Wuorinen[1] point out that, in order to secure the best separation, the concentration of the free phthalic acid should be such that hydrolysis will begin at about 55° C. A small portion of the solution should be heated to determine the temperature at which the hydrolysis begins; if below 50°, more phthalic acid should be added, or, if above 60°, ammonium hydroxide should be added to neutralize the excess phthalic acid.

The phthalates, diluted so that there were about ten grams of oxide for each liter of solution, were heated on a steam bath, the flask being shaken frequently to ensure uniform heating of the solution. For the first fraction, the temperature was raised gradually up to 50°C. and the basic phthalates were filtered off in the form of a flocculent precipitate. The precipitate was treated with nitric acid which liberated phthalic acid and gave a solution of the earth nitrates that could easily be filtered from the free acid. The earths were precipitated as oxalates and ignited to oxides. The second fraction was

1. Loc.cit.

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obtained by heating the solution to 62°C. The atomic weight, the temperature to which the solution was heated, and the weight of the oxide of each fraction is given in the following table:

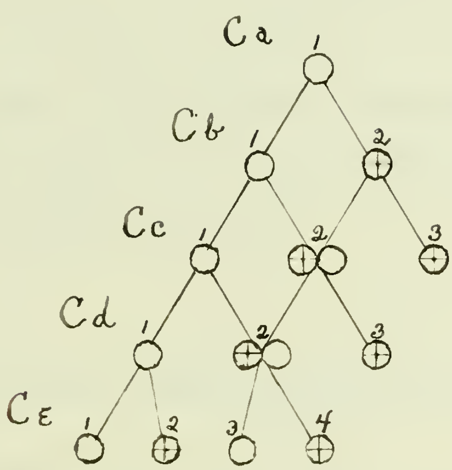
Table I.

Number	Temp. Limit	Weight of Oxide	Atomic Weight
1	50°	8.2 g.	100.8
2	62°	3.8	101.6
3	71.5°	3.0	100.5
4	75°	.5	99.3
5	80°	5.0	99.6
6	90°	---	-----
7	--	12.	94.5

Fraction 7 was precipitated by the addition of ammonium hydroxide; fraction 6 was lost; fraction 1 should contain material of a higher atomic weight than fraction 2, but the difficulty of securing a uniform heating throughout the solution makes it possible that such anomalies may occur.

In order to test the method further, fractions 1 to 5 inclusive were united to form fraction C b 1, while fraction 7 constituted C b 2. Each of these fractions was hydrolyzed in the manner described above except that only two fractions were obtained from each, a hydrolyzed and an unhydrolyzed portion. The temperature was brought up to 85°or 87° C. The hydrolyzed portion of Cb 1 became Cc 1, while the unhydrolyzed portion

of Cb 1 and the hydrolyzed portion of Cb 2, became Cc 2. The basic phthalate precipitate of the hydrolyzed portion of Cb 2 was treated with nitric acid, filtered from the phthalic acid, and precipitated with ammonium hydroxide. The washed hydroxides were dissolved in the unhydrolyzed portion of Cb 1, enough phthalic acid being used to secure solution. The unhydrolyzed portion of Cb 2 was converted to the oxide and weighed as Cc 3 Further operations may be indicated by the accompanying diagram. Each circle enclosing a cross represents a hydrolyzed portion, and the other circles represent the unhydrolyzed portions.



Fraction Cd 3 was set out of the series as Cc 3 had been. The weights of the oxide and the mean atomic weight of the four fractions in the last series as well as the two fractions set out, were as follows:

Table II.

Number	Weight of Oxide	Atomic Weight
Ce 1	2.0g.	107.7
Ce 2	3.0	104.7
Ce 3	4.0	101.5
Ce 4	5.3	96.7
Cd 3	11.5	94.9
Cc 3	4.5	92.3

The original material used in this fractionation had an atomic weight of 97.7, or a holmium content of 25.4 percent. The oxide of fraction Cc_3 still retained a slight yellow color, while in a four liter solution only one holmium line, λ = 536 , was visible; Ce_1 was a light cream color, and the solution showed a strong holmium absorption.

VIII. Fractional Precipitation with Sodium Nitrite.

Hopkins and Balke[1] used, for the purification of yttrium, a method suggested by Holden and James[2] which consists in a fractional precipitation by sodium nitrite from a dilute neutral nitrate solution. This method has been used in this laboratory for the purification of erbium from yttrium,[3] and, because of the comparatively slight difference in the basicity of holmium and erbium, it was thought that the method could be

1. Journ. Amer. Chem. Soc., 38, 2332 (1916)
2. Journ. Amer. Chem. Soc., 36, 1419 (1914)
3. E. Wichers, Doctor's Thesis, University of Illinois, (1917)

[illegible]

[illegible]

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applied to the purification of holmium from yttrium.

Material for this fractionation was obtained from the bromate series mentioned above. The oxide, approximately one hundred grams, was dissolved in nitric acid, and the solution evaporated to drive off the excess acid. After dilution to about eight liters, sixty grams of sodium nitrite, dissolved in a small volume of water, were added. The solution was heated as hot as possible on a steam bath and finally brought to boiling by passing in a vigorous blast of steam. Upon boiling for a few minutes a cloudiness and later a rather granular precipitate formed that was easy to filter and wash. It was noticed that the steam escaping from the flask during the process of boiling had an acid reaction toward litmus, while the solution was slightly alkaline. The average time of boiling for each precipitation was one hour. This method gave the following series:

Table III.

Number	Weight of Oxide	Atomic Weight
1	4.7 g.	98.1
2	5.0	97.3
3	12.0	95.9
4	5.0(a portion lost)	94.0
5	12.0	94.3
6	12.7	91.5
7	15.5	90.9
8	16.1	90.6
9	6.5	88.7
10	.5	89.2

The atomic weight, absorption spectrum, and color showed fraction 9 to be almost pure yttrium. It is supposed that the presence of some of the colored earths of the cerium group caused the color and slight increase in atomic weight in the last and most basic fraction. The atomic weight of the original material 92.3 indicated a holmium content of about 4.8 percent, while the 98.1 of the first fraction shows that it is 12.5 percent holmium, an increase of 250 percent in holmium content.

The same method of fractionation was applied to the material of the same holmium content as that used in the fractional hydrolysis of the phthalates. As the series was smaller, forty grams of sodium nitrite were used for the precipitation of each fraction, instead of the sixty grams of the larger series. The following results were obtained:

Table IV.

Number	Weight of Oxide	Atomic Weight
1	1.8 g.	103.3
2	2.5	102.4
3	3.5	101.3
4	5.4	94.4
5	3.7	93.1
6	3.6	91.3

The atomic weight of the first fraction,103.3,indicates a holmium content of 19.5 percent, the original material having 12 percent. The separation is not as rapid in this series as

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in the former, possibly because of the smaller sample.

This method of fractionation was also tried on three fractions of a bromate series run by another worker in this laboratory.[1] The absorption spectrum of the combined fractions indicated the presence of holmium, dysprosium, praseodymium, and neodymium; the atomic weight, 128.3, showed that yttrium was present, while the light brown color of the oxide was probably due to the presence of a small amount of terbium. The fractionation carried out in the manner described above gave the following results:

Table V.

Number	Weight of Oxide	Atomic Weight	Absorption showed
1	10.8 g.	143.7	Ho,Dy.
2	13.0	138.9	Ho,Dy,Pr,Nd.
3	16.1	134.8	Ho,Dy,Pr,Nd.
4	14.2	131.2	Ho,Dy,Pr,Nd.
5	10.9	123.5	Ho,Dy,Pr,Nd.
6	6.6	114.3	Ho,Dy,Pr,Nd.
7	3.2	111.8	Ho,Dy,Pr,Nd.

Sixty grams of sodium nitrite were added for the precipitation of each fraction. Fraction 1 was a cream color; the color increased in intensity to the light brown of fraction 6; and fraction 7 was a dark reddish brown, when ignited in the air, and a light gray, when ignited in a stream of hydrogen. While fraction 2 showed very faint lines of praseodymium and neodymium in its absorption spectrum, the intensity of the absorp_

1. H.C. Kremers, Doctor's Thesis. University of Illinois (1917)

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[illegible]

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tion increased progessively through the series. A concentrated nitrate solution of the last fraction was colored green and its absorption spectrum showed the presence of a rather large amount of praseodymium. However, since Pr_4O_7 is black, the brown color of the oxide showed that terbium was present in large amounts. There was a change of 0.73 percent in the weight of the oxide before and after heating in a stream of hydrogen. Assuming all of the higher oxide found to be Tb_4O_7, it was calculated that there was present approximately 30 percent of terbium. The presence of a small amount of dysprosium in each of the fractions showed that holmium cannot be freed from dysprosium by this method.

IX. Summary.

1.- Earth material from gadolinite was separated into the cerium and yttrium groups. The yttrium group material was purified from cerium and converted into bromates, preparatory to fractionation.

2.- By means of four series of fractional hydrolysis of the phthalates the holmium content of a holmium-yttrium mixture was increased from 12 percent to 25.4 percent.

3.- One series of fractional precipitation with sodium nitrite increased the holmium content 250 percent in material poor in holmium. The color of the oxide of the least basic fraction of a series containing holmium, dysprosium, praseodymium,neodymium, yttrium, and terbium, indicated that the terbium was about all removed and the absorption spectrum failed to reveal traces of

either neodymium or praseodymium. The color of the oxide and absorption spectrum of the most basic fraction showed a concentration of terbium, praseodymium, and neodymium. Dysprosium cannot be removed by this method.

4.- The fractional precipitation with sodium nitrite is considered the better of the two methods,(a) because the chemicals employed are cheaper, (b) because it is easier of operation, (c) and because an oxide of higher holmium content was obtained by one series of fractional precipitation with sodium nitrite than was obtained from material of the same atomic weight by one series of fractional hydrolysis of the phthalates.